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MRL-R-798 ✓

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

MATERIALS RESEARCH LABORATORIES

MELBOURNE, VICTORIA

REPORT

MRL-R-798

SURFACE MODIFICATION CONCEPTS FOR ENHANCEMENT OF
THE HIGH-TEMPERATURE CORROSION RESISTANCE
OF GAS TURBINE SUPERALLOYS

Noel A. Burley

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hot corrosion and extend their useful lives.

A concept is presented that the high-temperature corrosion
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DOCUMENT CONTROL DATA SHEET

1. DOCUMENT NUMBERS:	2. SECURITY CLASSIFICATION:
a. AR Number: AR-002-382	*a.* Complete document: UNCLASSIFIED
b. Series & Number: REPORT MRL-R-798	*b.* Title in isolation: UNCLASSIFIED
c. Report Number: MRL-R-798	*c.* Abstract in isolation: UNCLASSIFIED

3. *TITLE:* SURFACE MODIFICATION CONCEPTS FOR ENHANCEMENT OF THE HIGH-TEMPERATURE CORROSION RESISTANCE OF GAS TURBINE SUPERALLOYS

4. PERSONAL AUTHOR(S):	5. DOCUMENT DATE: DECEMBER 1980
BURLEY, Noel A.	6. TYPE OF REPORT & PERIOD COVERED:

7. CORPORATE AUTHOR(S):	8. REFERENCE NUMBERS:
Materials Research Laboratories	*a.* Task: DST 77/064
	b. Sponsoring Agency: Defence (DSTO)
	9. COST CODE: 55 4860

10. IMPRINT (Publishing establishment)	11. COMPUTER PROGRAMME(S): (Title(s) and language(s)):
Materials Research Laboratories, P.O. Box 50, Ascot Vale, Vic. 3032 DECEMBER 1980	

12. RELEASE LIMITATIONS (of the document):

Approved for public release

12-0. OVERSEAS: N.O. ☐   P.R. ☐1   A ☐   B ☐   C ☐   D ☐   E ☐

13. ANNOUNCEMENT LIMITATIONS (of the information on this page):
No limitations

14. DESCRIPTORS: 630 / Gas turbine blades / Diffusion coatings //
636 / Hot corrosion // 645 / Nickel alloys : Cobalt alloys : Superalloys :
Aluminide coatings : Cathodic protection : Corrosion resistant alloys : Hot
end aerofoil components : Laser surface alloying : Surface modification //

15. COSATI CODES: 1113

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This report summarizes the current view of the mechanisms of the phenomenon of hot corrosion, whereby the surface integrity of gas turbine superalloys is degraded, and also the principal types of protective coating applied to aerofoil components made of these materials to inhibit hot corrosion and extend their useful lives.

A concept is presented that the high-temperature corrosion resistance of superalloys can be significantly enhanced by selective modification of the composition and structure of their parasurface zones, utilizing new methods of surface treatment such as ion implantation, laser alloying, and thermal passivation.

C O N T E N T S

SURFACE MODIFICATION CONCEPTS FOR ENHANCEMENT OF THE

HIGH-TEMPERATURE CORROSION RESISTANCE OF GAS TURBINE SUPERALLOYS

1. INTRODUCTION

1.1 Military propulsion technology involves two natural resources – materials and energy, and these are inextricably linked. Just as technological materials cannot be produced, converted or utilized without energy, neither can energy without specialized materials. This interdependence is ever intensifying, and the technical problems of energy conversion are largely those of materials. In this field the design engineer is materials limited, and the severity of this restriction increases as projected use temperatures are increased. In few other energy conversion devices are efficiency increases so restricted by materials than in gas turbines such as are used for advanced military propulsion engines. In these systems development is limited by the Carnot efficiency relation; hence there is a continual quest for ever-increasing operational temperatures.

1.2 Since World War II, the gas turbine has experienced continuing development as a highly efficient propulsion unit for state-of-the-art jet aircraft, both civil and military, where thrust/weight ratios are of paramount importance. In more recent times the gas turbine has been adapted for naval ship and battle tank propulsion.

1.3 Gas turbines have power/density and energy/density ratios (Figure 1) that exceed those of all practical energy converters. Further progress in the development of aeroengine gas turbines depends primarily on the ability of materials engineers and scientists to devise materials with improved strength/weight ratios at higher temperatures. Such new or improved materials must also possess adequate resistance to fatigue, corrosion and shock. For marine and land gas turbines, weight and size considerations tend to be less significant, but corrosion resistance and metallurgical stability assume greater importance.

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1.4 Whilst the conventional turbine alloys still continue to offer some scope for enhancement by means of alloying and processing techniques [2], significant advances depend increasingly upon the incorporation of new classes of materials such as ceramics and composites. The continuing need is for materials that will withstand even higher temperatures. Although the upper temperature limit for metallic alloys has increased steadily by an average of 10°C per year over the past thirty or so years [1], the potential for further increases with existing or proposed metallic alloys must now be small.

1.5 Although engineers have shown a continuing reluctance to design for turbines with ceramics which they class as brittle materials [3], in recent years there has been a significant change in the attitude of the gas-turbine engine manufacturing community toward ceramic materials [2]*. There seems little doubt that, provided problems of mechanical properties can be satisfactorily surmounted, ceramic materials could be used in uncooled (or significantly less cooled) gas turbines to increase Carnot cycle efficiency, thrust/weight ratios, and corrosion/erosion resistance.

1.6 Progressive advances in blade cooling techniques, particularly by internal ducting, over the past decade have permitted further increases in turbine inlet-temperatures. Nevertheless, with present increases in compressor-air temperatures and the quantity of air to be ducted, the rate of further increase in effectiveness of air cooling is now diminishing [4].

1.7 It is generally accepted that the alloying requirements for high-temperature corrosion resistance and for high creep strength are so different that protective coatings, such as aluminized layers or special alloys like Co-Cr-Al-Y, will always be required for high-temperature corrosion resistance in high-strength alloys. The objective view of coatings, however, must be that they offer purely temporary assistance, mainly in life extension, without any real hope for significant improvement in the operational temperatures of gas turbine superalloys.

1.8 Existing types of superalloys, which are mainly nickel-based**, appear

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* Thermal-shock resistant ceramics such as Si_3N_4, SiC and 'LA5' (glass-ceramics) are now developed to the point where they could be considered as true engineering materials.

** Nickel-based alloys are used for turbine blading and nozzle guide-vanes. Cobalt-based alloys are now largely confined to nozzle guide-vanes, particularly in marine gas turbines [4]. An example of a nickel-based turbine superalloy is NIMONIC 115 (a trademark of H. Wiggins & Co. Ltd., Hereford, England) which is –

$$Ni-15Cr-15Co-5Al-4Ti-1Fe-.15C-.15Zn-.02B \ (wt.-\%)$$

likely to be used in commercial gas turbine engines for the foreseeable
future. Although it is not realistic to consider it in isolation of other
fundamental properties, the high-temperature corrosion resistance of
superalloys is a continuing prime concern. Thus, the factors discussed so
far imply the existence of a strong case for the development of new methods
for enhancing the high-temperature surface-degradation resistance of
superalloys, methods which may hopefully permit the use of these materials
at higher upper operating temperatures.

1.9 This report describes in summary the phenomenon of hot corrosion,
whereby the surface integrity of gas turbine superalloys is degraded, and
also the principal types of protective coating applied to these materials
to inhibit hot corrosion and extend the useful lives of aerofoil
components. It also presents the concept that the high-temperature
corrosion resistance of superalloys can be significantly enhanced by
selective modifications of the composition and structure of their
parasurface zones, utilizing new methods of surface treatment such as
thermal passivation, ion plating, ion implantation and others.

2. HOT CORROSION

2.1 Introduction

Implicit in the design of modern gas turbine engines is the premise
that their aerofoil components, made of nickel- and cobalt-based
superalloys, will maintain both mechanical and surface integrity for
substantial periods of time in a variety of gaseous environments which are
oxidizing at high temperatures. The ability of such components to
maintain their surface integrity is a function of certain properties of the
alloys from which they are made, including resistance to cyclic oxidation
and hot corrosion and to thermal fatigue cracking and corrosion fatigue.
This report is concerned with the degradative process of hot corrosion.

Hot corrosion can be described as a process of accelerated oxidation
which results when materials are exposed to combustion environments which
involve the deposition of ash or salts upon their surfaces. Generally,
the presence of such deposits causes the nature of the reactions occurring
between the materials and the combustion gases to be substantially
different from those occurring in the absence of the deposit. Hot
corrosion is a principal process of degradation of aerofoil surface
integrity in gas turbine engines.

2.2 Mechanisms of Hot Corrosion

Because of the severe penalties which hot corrosion degradation in
gas turbines can impose upon the operational and maintenance economics and
the tactical efficiencies of military vehicles which they propel,
considerable scientific effort has gone into determining the mechanisms by
which this process degrades high-temperature alloys [e.g. 5-18]. A review

of these labours may suggest that various degradative mechanisms proposed by the various investigators are inconsistent.

Giggins and Pettit [19], however, have presented a unified theory of hot corrosion in which they assert that this degradative process can occur via different mechanisms depending upon the conditions, and that these various mechanisms and the effects produced by different alloying elements are, in fact, not inconsistent. They propose that the hot corrosion attack of alloys consists of an initiation stage and a propagation stage; during the initiation stage the attack is similar to that occurring between the gas and the alloy in the absence of the deposit, but the alloys are being preconditioned in a way that determines the particular propagation mode that will cause the degradation.

2.2.1 The Initiation Stage

During this stage, elements in the alloy are oxidized by mechanisms similar to those which would have operated in the absence of the deposit, and a reaction-product barrier forms beneath the deposit on the alloy surface. The time for which the reaction-product barrier is stable beneath the surface layer (e.g. salt) is influenced by a number of factors [19] the more important of which are discussed briefly below. These factors are important in that they pre-condition the alloy, thus determining the subsequent propagation mode which will be followed.

2.2.1.1 Alloy Composition

The effects of alloy composition on the initiation stage are legion and space limitation permits only the citing of some cases involving the major alloying elements chromium and aluminium.

For example, the duration of the initiation stage for hot corrosion induced by sodium sulphate, Na_2SO_4*, in air is increased as the aluminium content of $Ni/Co-(15$ to $25)Cr-nAl-0.5Y$ is increased from n=(5 to 10) wt.-%. (The initiation stage for the Co-based alloys is longer than that for the Ni-based alloys.) The higher aluminium contents produce $\alpha-Al_2O_3$ scales which are stable for longer times prior to the imposition of a propagation mode mechanism.

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* It is usually proposed [e.g. 19] that, since Na_2SO_4 is the most common extraneous deposit identified on aerofoil components of gas turbines and since sodium and chloride ions are the preponderant components of the common ingestant sea-salt, the gas-phase reaction –

$$2NaCl + SO_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl,$$

followed by the condensation of Na_2SO_4, accounts for the deposition of the corrosive salt on the aerofoil surface.

Again, for example, increasing the chromium content of Ni-nCr-6Al from n = (8 to 15) wt.-% causes the initiation stage for hot corrosion, induced by large amounts of Na_2SO_4 in air, to be substantially increased. As before, the increasing stability of the external scales of both Cr_2O_3 and Al_2O_3 are the cause. A similar result is obtained if the aluminium content of this alloy is increased above 6 wt.-%.

These scales affect the subsequent relevant propagation mode (namely basic fluxing, in which it is necessary for a substantial oxygen gradient to be established across the Na_2SO_4 deposit - see section 2.2.2.1) because the scales formed on alloys of the higher chromium/aluminium concentrations remain stable longer and consume less oxygen than those which are discontinuous, as when formed on alloys of the lower concentrations.

2.2.1.2 Gas Composition

The composition of the gas phase significantly influences the initiation and degradation rate of hot corrosion attack. For example, in the oxidation at 700°C of Co-Cr-Al-Y coated with Na_2SO_4, hot corrosion attack is initiated virtually from the beginning when sulphur trioxide, SO_3, is present in the gas, but only after a substantial initiation period if the gas is pure oxygen. This occurs because, even though Na_2SO_4 is not liquid at 700°C, when SO_3 is present a liquid solution of $Na_2SO_4-CoSO_4$ is formed, and hot corrosion is more easily induced when a liquid phase is present.

The influence of SO_3 on the subsequent propagation mode (acidic fluxing - in which the corrodent deposits are made acidic - see section 2.2.2.1) is that the degradative attack becomes self sustaining.

2.2.1.3 Gas Velocity

Gas velocity effects, which are significant in the hot corrosion of alloys, are especially evident where volatile components are active ingredients in the corrosion process.

For example, in the isothermal hot corrosion, at 1000°C, of Ni-8Cr-6Al-6Mo coated with Na_2SO_4 the attack of this alloy is initiated in static air much sooner than in flowing oxygen. The accumulation of MoO_3 in Na_2SO_4 accelerates hot corrosion and, in the case in point, less MoO_3 is lost from the Na_2SO_4 to the gas in the static environment.

2.2.1.4 Salt Composition

Here there are two different effects both related to progressive changes in salt composition. On the one hand the deposit may transform from solid to liquid with the compositional change and, as stated above, hot corrosion is more easily induced when a liquid phase is present. On the other hand a change in salt composition can cause a change in the mechanism of attack. For example, degradation becomes more severe as the concentration of NaCl in Na_2SO_4 increases, and the NaCl also causes the mechanism of hot corrosion in the propagation phase to be different to that

induced by pure Na_2SO_4.

2.2.1.5 Temperature

Hot corrosion processes are dependent upon temperature. In many cases the duration of the initiation phase decreases as the temperature increases. Hot corrosion conditions do exist, however, where the attack becomes less severe as the temperature is increased. One reason for this is that the condensation rate of gaseous Na_2SO_4 decreases with increasing temperature. Some generalized reaction/temperature relationships are given in Figure 2.

Even if the salt deposition rate is constant, other conditions govern a greater rate of attack for lower temperatures. For example, the deposit may be liquid at lower temperatures but solid at higher temperatures, as may be expected when Na_2SO_4 is in contact with oxides of nickel or cobalt and sulphur trioxide in the gas. At low temperatures (~ 650°C) the SO_3 pressure can be sufficient to form a liquid Na_2SO_4-$CoSO_4$ solution, whereas at higher temperatures (~ 850°C) the amount of $CoSO_4$ in the Na_2SO_4 may not be sufficient and the deposit will be solid.

In the propagation phase SO_3 plays a significant role in the corrosion process. Hot corrosion, with Na_2SO_4 deposits and a constant pressure of SO_3 in the gas, can occur faster at 700°C than at 1000°C. For a fixed amount of sulphur in the gas the SO_3 pressure decreases as the temperature is increased, and this causes a slower hot corrosion rate at the higher temperatures.

Temperature- or thermal-cycling during the initiation stage has a controlling influence on subsequent hot corrosion because the reaction-product barrier that forms during the reaction of the alloy with the gas may crack or spall. The transition from initiation to propagation mechanisms therefore occurs sooner the larger the number of cycles.

2.2.1.6 Erosion

The initiation stage duration is reduced when erosive conditions are present. Particle impact damage to the oxide produces virtually the same effects as thermal cracking. In the propagation stage erosion accelerates hot corrosion by ejecting porous scale which would otherwise absorb corrodent salts.

2.2.1.7 Other factors

Other factors can influence the duration of the initiation stage [19]. Among the more important of these are the fabrication condition and component geometry. These are not discussed here.

2.2.2 The Propagation Stage

As is obvious from section 2.2.1, there are a number of factors which affect the initiation of hot corrosion, and these pre-condition the alloy

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for the onset of the propagation stage.

The propagation stage of hot corrosion can be considered in three categories [19] -

    (i)   The salt is innocuous and degradation proceeds by the mechanism determined by the ingredients, alloy and gas. Such a situation can occur with porous solid deposits through which the gas can readily permeate.

The other two categories involve degradation mechanisms which are different from those that occur in the absence of salt deposits.

    (ii)   The salt deposit, or a product of the salt-alloy-gas reaction, is liquid. Reaction between elements in the alloy and components of the gas in the presence of the liquid results in the formation of non-protective reaction products. This category of propagation reaction has been labelled 'salt fluxing reactions'.

    (iii)   A component of the salt is added to the alloy, or reacts with the alloy or its corrosion products in such a way that non-protective reaction product barriers are developed. This category can be called salt component-induced hot corrosion, or 'salt component-alloy reactions'.

The propagation modes (ii) and (iii) above are discussed below in summary in terms of the effects produced by the salt Na_2SO_4, the predominant component of deposits initiating hot corrosion.

2.2.2.1 Salt Fluxing Reactions

The various reactions by which hot corrosion by salt fluxing can occur are summarized in Table 1. In this table, variation 'A' covers the basic processes that occur due to the production of oxide ions in the Na_2SO_4 deposit, as a result of the removal of oxygen and sulphur from the Na_2SO_4 by the alloy. The hot corrosion attack may occur because of the continuous solution of oxide in the Na_2SO_4 (variation 'A-1'), or because of its solution and reprecipitation (variation 'A-2'). In both cases the attack is not self-sustaining, but rather is controlled by the amount of Na_2SO_4. A supply of SO_3 is required for the attack to proceed indefinitely, otherwise attack will stop when the melt becomes sufficiently basic at the precipitation site. Variation 'B' covers the Rapp-Goto model [20], where hot corrosion attack does not require sulphur removal from the melt, but occurs because of a negative solubility gradient of the corrosion product in Na_2SO_4.

Variations 'C', 'D', 'E' and 'F' (Table 1) cover the acidic salt fluxing processes, where the acidic component comes from the gas phase. Variation 'F' is the same type of process but the acidic component comes from the alloy. Variation 'E' covers the Rapp-Goto concept for acidic melts.

2.2.2.2 Salt Component-Alloy Reactions

A variety of elements from the deposited salt can be introduced into the corrosion product or the surface regions of the alloy, and eventually affect their oxidation behaviour.   In the case of Na_2SO_4 and NaCl deposits, the significant elements are sulphur and chlorine.   Carbon is also important since fuel combustion usually produces a hot-corrosion environment.   The effects produced by each of these elements is now considered in turn -

Sulphur-Induced Hot Corrosion

The oxygen pressure in Na_2SO_4 deposits at the alloy/Na_2SO_4 or oxide/Na_2SO_4 interfaces can be very low.   When this is so the pressure of sulphur, due to sulphur in the gas as well as in the deposit, is usually high enough to form sulphides of aluminium and chromium and, in some cases (unless the SO_3 pressure is very low), sulphides of cobalt, nickel and iron.   The accumulation of these sulphides in the alloy can greatly exacerbate degradation during subsequent oxidation.   A generalization is that nickel-base high-temperature alloys with aluminium contents of at least (6 to 12) wt.-% are relatively resistant to this type of attack; degradation occurs only after the aluminium content has been reduced by oxide spallation induced by thermal cycling.

Sulphur-induced hot corrosion causes accelerated oxidation as a result of the formation of less-protective oxide scales, which process occurs by at least three different mechanisms -

    (i)   The oxidation of aluminium and chromium dissolved in sulphides of nickel or cobalt results in the production of discontinuous scales (of Al_2O_3 and Cr_2O_3).

    (ii)   The conversion of certain sulphides to oxides of smaller volume produces non-protective scales.

    (iii)   Selective oxidation to produce protective scales is adversely retarded when inward diffusing sulphur reacts with outward diffusing elements which would otherwise react with oxygen at the surface to produce the scale.

Chloride-Induced Hot Corrosion

Very small concentrations of NaCl, as little as 5 ppm, in the surface deposits or in the gas phase cause stress-spallation of the oxide scales to occur more readily [20].   Chloride ions are observed to concentrate at the oxide-alloy interface, but otherwise the mechanism for decreased scale adhesion seems little understood [19].

Whilst the above effect is significant, another process again of hot corrosion attack occurs at higher chloride concentrations, e.g. one

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wt.-%. The following sequence of reactions has been hypothesized [19] -

$$x(Na_2SO_4 + NaCl)_{liq.} + 2(Al, Cr)_{alloy} \rightarrow$$

$$Al_2O_3 + Cr_2O_3 + CrS + y(Na_2SO_4 + NaCl)_{liq.} \qquad ....(1)$$

$$NaCl + 2Al_{alloy} + O_2 \quad \rightarrow \quad NaAlO_2 + AlCl \qquad ....(2)$$

$$2AlCl + \tfrac{3}{2}O_2 \quad \rightarrow \quad Al_2O_3 + Cl_2 \qquad ....(3)$$

$$Cl_2 + 2Al_{alloy} \quad \rightarrow \quad 2AlCl \qquad ....(4)$$
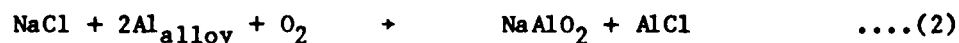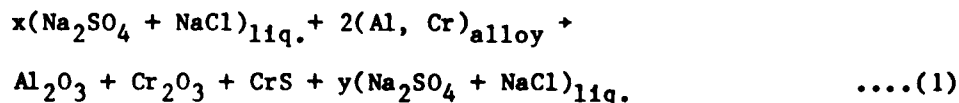
Eqn.(1) suggests that the melt adjacent to the alloy can become enriched in NaCl due to the formation of the oxides and sulphides. The NaCl component of the $(Na_2SO_4 + NaCl)$ melt may then begin to react locally with the components of the alloys, as proposed by eqn. (2). The metallic chloride could then be converted by inward-moving oxygen (eqn. 3), and the chlorine re-cycled to react with elements in the alloy (eqn. 4). At least some features of this hypothesis have been substantiated by metallographic evidence. The surface depletions in chromium and aluminium caused by this process have deleterious consequences which are obvious.

2.2.2.3 Carbon-Induced Effects

The combustion environment of a gas turbine can lead to deposits of carbon and unburned fuel which will result in a lowering of the oxygen pressure over the alloy component surfaces. This, in turn, leads to a greater susceptibility to effects produced by other gas-phase components such as sulphur, carbon and nitrogen, especially when salt layers are present on the surface. Elements in the alloy then tend to react more readily with the sulphur in these layers [22] which, as a consequence, are enriched in oxide ions.

Hence, the propagation mechanisms of hot corrosion attack which are influenced by these reducing conditions are those of the basic-fluxing and sulphur-induced modes. Further, the attack induced by chlorides (section 2.2.2.2) is especially effective when the oxygen pressure at the salt-alloy interface is low [19]; such attack is therefore greatly enhanced when it occurs in combination with carbon deposits and/or excess fuel.

2.2.2.4 Interaction Between Different Propagation Modes

Interaction between the various propagation modes for Na_2SO_4 induced hot corrosion attack is quite common. One particular degradation mode may be dominant for short exposure periods, and another after extended exposure; and the dominant mode can change with variation of temperature. These interactions, which must be taken into consideration when identifying alloys which are degraded by particular propagation modes, have been discussed in detail [19].

T A B L E 1*

POSSIBLE SALT FLUXING REACTIONS FOR Na_2SO_4 DEPOSITS
ON ALLOYS

Basic Processes

A. Dissolution of Reaction Product, (i.e. AO) Due to Removal of Sulphur and Oxygen from the Na_2SO_4 by the Metal or Alloy:

$$SO_4^{2-} \text{ (sulphate} \rightarrow \frac{1}{2}S_2 \text{ (for reaction} + \frac{3}{2}O^{2-} \text{(for reaction} + O^{2-} \text{ (for reaction}$$
$$\text{deposit)} \qquad \text{with alloy)} \qquad \text{with AO)}$$

Reaction between AO and oxide ions can follow two courses:

(1) Continuous dissolution of AO

$$A\text{(alloy)} + \frac{1}{2}O_2 + O^{2-} \rightarrow AO_2^{2-}$$
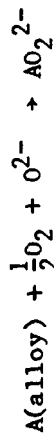
Na_2SO_4 is converted to Na_2AO_2 and attack is dependent on amount of Na_2SO_4 initially present.

(2) Solution and reprecipitation

$$A\text{(alloy)} + \frac{1}{2}O_2 + O^{2-} \rightarrow AO_2^{2-} \text{ (solution)} \rightarrow AO \text{ (precipitate)} + O^{2-}$$

A supply of SO_3 is required in order for attack to proceed indefinitely, otherwise attack will stop when melt becomes sufficiently basic at precipitation site.

B. Solution and Precipitation of AO as a Result of a Negative Gradient in Solubility of AO in Na_2SO_4.

_____

* after [19]

T A B L E 1 (Cont'd)

Acidic Processes

Gas Phase Induced

C. Formation of ASO_4 in Na_2SO_4:

$$A(alloy) + SO_3 + \frac{1}{2}O_2 \rightarrow A^{2+} + SO_4^{2-}$$

Continuous solution of ASO_4 in Na_2SO_4 requires continuous supply of SO_3 and O_2 from gas.
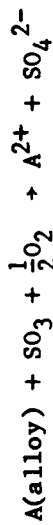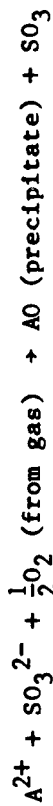
D. Solution and Precipitation of AO in Na_2SO_4 Due to Reduction of SO_3:

$$A(alloy) + SO_3 \text{ (from gas)} \rightarrow A^{2+} + SO_3^{2-} \text{ (in melt)}$$

$$A^{2+} + SO_3^{2-} + \frac{1}{2}O_2 \text{ (from gas)} \rightarrow AO \text{ (precipitate)} + SO_3$$
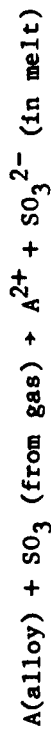
E. Solution and Precipitation of AO as a Result of a Negative Gradient in Solubility of AO in Na_2SO_4 as in B.

Alloy Phase Induced

F. Solution of AO in Na_2SO_4 Modified by Second Oxide from Alloy (i.e. BO_3).

- Modification of Na_2SO_4 by BO_3

$$B(alloy) + \frac{3}{2}O_2 + SO_4^{2-} \rightarrow BO_4^{2-} + SO_3$$
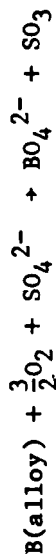
- Solution reaction for AO, Na_2SO_4 becomes enriched in ABO_4

$$A(alloy) + B(alloy) + 2O_2 \rightarrow A^{2+} + BO_4^{2-}$$
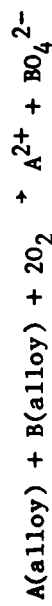
- Solution-Precipitation

$$A(alloy) + B(alloy) + 2O_2 \rightarrow A^{2+} + BO_4^{2-} \rightarrow AO + BO_3$$
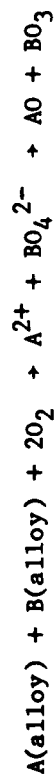
Precipitation of AO in Na_2SO_4 as a result of loss of BO_3 from Na_2SO_4 permits substantial attack with small amounts of Na_2SO_4.

3. PROTECTIVE COATINGS

3.1 Introduction

Gas turbine technology has reached a stage where the conventional nickel- and cobalt-based superalloys used for hot-end aerofoil components (rotor blades and nozzle guide vanes) can no longer cope with the ever increasing temperatures and severity of environmental conditions to which they are subjected. The protective coatings which consequently are routinely applied to these components to inhibit hot corrosion are essentially of two classes -

      (1)   diffusion aluminide layers, and

      (2)   M-Cr-Al-Y overlays (M $\equiv$ Ni, Co, Fe)

The first class of coating involves the high-temperature interdiffusion of aluminium into the alloy to form intermetallic compounds, such as NiAl, which have enhanced abilities to form the protective scale Al_2O_3. Variants of this class include individual or multiple additions of chromium, silicon, tantalum, and the noble metals platinum and rhodium, which give even further enhancement of hot corrosion resistance.

The second class of coating involves the deposition of alloy overlays by physical vapour-deposition methods involving only limited interdiffusion between coating and substrate to facilitate bonding.

3.2 Coating Methods

It is not within the scope of this paper to discuss the considerable variety of processes available for depositing protective coatings onto the aerofoil surfaces of turbine components. Some of these processes, which range from the traditional paint, dip and electroplating methods through chemical vapour-deposition to physical vapour-deposition techniques, have reached full commercial status for engine applications while others are in the research and development stage. Several good reviews of these coating processes exist in the literature [e.g. 23] to which the reader is referred.

3.3 Diffusion Aluminide Layers

This type of coating, which is extensively used to protect blades in military turbines where the combined conditions of temperature and environment are not too aggressive, is relatively cheap and easy to apply, and can be stripped from components during overhaul prior to re-aluminizing.

Virtually all diffusion aluminide coatings consist of the intermetallic compounds NiAl and/or CoAl located in the parasurface regions of nickel- and cobalt-based superalloys. Two archetypal varieties of coatings, which may be defined as 'inward-diffusion' and

'outward-diffusion' [24], are illustrated in Figure 3. The former (inward) type contains all the elements of the base alloy in the layer, either in solution in the MAl (M ≡ Ni or Co) phase or as precipitated phases. It is formed by the predominant inward diffusion of aluminium from coating media of sufficiently high aluminium activity to cause formation of δ-phase (Ni_2Al_3). Subsequent stabilizing heat treatment causes some outward diffusion of nickel to form a three-zone β-phase (NiAl) coating. The latter (outward) type of coating contains the elements of the base alloy only to their usual low limit of solubility in the MAl phase; it is formed by predominant outward diffusion of nickel from the substrate alloy to react with aluminium of suitable activity to stabilize the β-phase (NiAl) of composition through which only nickel can diffuse. This process produces a two-zone β-phase coating. In both types of coating, the inner diffusion zone, consisting of precipitates of carbides and δ-phase in a NiAl matrix, is formed by the outward diffusion of nickel from, and the resulting enrichment of aluminium in, the substrate alloy.

The morphology and composition of these coatings vary in many complex ways, and these variations exert substantial influences on the physical properties and oxidation resistance of the protective layers. It is beyond the scope of this paper to deal with these variations, and the reader is referred to published reviews [e.g. 38].

Conventional aluminide coatings are the yardstick by which other coatings are usually judged [23]. They are the traditional standard for protecting the hot components in most aero and marine gas turbines. In general, they can be relied upon to provide good resistance to high-temperature oxidation and thermal fatigue. The aluminium-rich surface layer acts as a reservoir for replenishing the protective alumina scale where loss by corrosion or rupture of the layer occurs.

Variants of aluminide coatings using individual or multiple additions of chromium, silicon, tantalum, and other elements have also been explored, but most interest is currently focussed [23] on the performance of diffusion coatings based on the addition of noble metals (platinum, rhodium) to aluminides. Both oxidation resistance and hot corrosion resistance are enhanced by the presence of these elements in the coating [24]. The platinum-modified aluminide coating system is applied by first electrolytically or otherwise depositing a platinum layer less than 10 μm thick [25], then pack-aluminizing the substrate to form an aluminide coating in the usual way [23]. The mechanisms by which the noble metal enhances coating resistance to high-temperature degradation are still the subject of active study, but hypothetical explanations include:-

(i)   the deposition of platinum prior to aluminization leads to a reduction or elimination, by diffusional control, of refractory elements in the outer region of the final coating [25];

(ii) the improved adherence of alumina scales [26]; and

(iii) enhancement of the Al_2O_3 scale by noble-metal doping [27].

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3.4 M-Cr-Al-Y Overlay Coatings

These coatings most commonly are applied commercially by electron beam vapour-deposition [see, e.g. 23]. In this process an alloy of the desired coating composition is vaporized by the impingement of a high-voltage electron beam and coatings are condensed from the vapour phase onto the aerofoil surfaces to desired thicknesses of about 100 μm. Coatings of virtually any M-Cr-Al-Y composition (M ≡ Co, Ni, Fe, or combinations thereof) can be produced to give, typically, a two-phase structure (MAl + M-Al solid solution) which is illustrated in Figure 4. They are designed to produce on heating in air either Al_2O_3 or Cr_2O_3 protective scales.

A virtue of the M-Cr-Al-Y coating is the degree of control which can be exercised over its properties [24]. Its ductility can be adjusted over a wide range by variation of the aluminium content and, in general, ductility is increased with increasing volume fractions of nickel or cobalt solid solution phases. Thus, increasing ductility is gained at the expense of oxidation and hot corrosion resistance which is dependent primarily on aluminium content.

Yttrium, which is present in the coating in fractional percentages, enhances resistance to high-temperature degradation by imparting increased oxide adherence. Hot corrosion resistance is also increased as chromium content increases. The presence of chromium increases the activity of aluminium [38] and allows external Al_2O_3 formation at an Al concentration lower than what is needed in a binary Ni-Al alloy (see section 4.3.2).

Compositions based on cobalt (Co-Cr-Al-Y) have the maximum resistance to sulphate-induced hot corrosion (see section 2.2.1.1). Platinum additions to this type of coating appear to provide potential for further improvement.

A considerable body of engine experience has been built up with electron-beam processed M-Cr-Al-Y coatings [23], with Ni-Cr-Al-Y compositions offering superior elevated-temperature oxidation resistance on nickel superalloys, and Co-Cr-Al-Y compositions offering better protection in the hot corrosion environment. Work to gain understanding of the basic mechanisms of the degradative processes in this class of coating has, unfortunately, fallen well behind the developmental and phenomenological experience [38].

3.5 Other Coatings

The most widely used and best established coating system is based on the aluminide compounds induced by the interdiffusion of aluminium (see section 3.3) whilst the overlay coatings (see section 3.4) offer an advantage, amongst others, over the aluminide types in that they cause minimal loss of mechanical properties (see section 3.7.1) through diffusion-consumption and loss of load bearing section of the substrate [23].

The broad property requirements of coatings for turbine aerofoil components include [23]:-

(i) high resistance to oxidation and hot corrosion,

(ii) adequate ductility to withstand changes in substrate dimensions without cracking,

(iii) compatibility with the base alloy in terms of constitution and thermal expansion,

(iv) low rate of interdiffusion between coating and substrate,

(v) ease of application to the base alloy, and

(vi) low cost in relation to life improvement.

As a result of attempts to optimize these property requirements, a range of variations on the basic diffusion aluminide and M-Cr-Al-Y overlay themes are emerging. Many of these are still in the research and development stage, whilst others are becoming commercially available, and many feature new methods of application (see section 3.2). They do not, however, introduce new primary concepts in the inhibition of high-temperature degradation processes beyond those already discussed under section 3 - Coatings. The newer variations include -

3.5.1 Chromizing and Siliconizing [23, 31, 32]

These coatings are applied using techniques similar to diffusion aluminizing. Although chromium-rich coatings offer some advantage over aluminides for hot corrosive environments, the chromia scales are less satisfactory than alumina scales at temperatures above about 850°C in high-velocity gas streams because of the greater volatility of chromium oxide.

The siliconizing process produces an oxidation resistant film (silica - SiO_2) on the surface of the coating in which the β-phase 'intermetallic' compound Ni_3Si predominates.

3.5.2 Combined Diffusion Coatings

In addition to simplex aluminized, chromized and siliconized coatings, duplex and complex combinations of these elements in coatings have been explored, and some, e.g. Cr-Al, Cr-Al-Si and Cr-Al-Ta [33], for example, have reached commercial status. Although these combined types of coating seem to have been proved cost-effective [23], interest in them has lately declined in favour of the noble-metal modified aluminides (section 3.3) and the M-Cr-Al-Y overlays (section 3.4).

A slurry applied coating of the combined diffusion type (designated SERMALOY J*) employs silicon and aluminium in a diffusion-type layer in

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* SERMALOY J is a tradename of the SermeTel Corporation of Pennsylvania.

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which it appears that the concentrations of aluminium and silicon at the surface are, respectively, about 30 wt.-% (about the same as in the simple aluminide coatings) and 10 wt.-%.

3.5.3 A Ni-Cr-Si Overlay Coating, applied by a proprietary plasma-spray process, is now available for industrial gas turbines [28].

3.5.4 A Crystalline MgO-Al$_2$O$_3$-SiO$_2$ Glass plus powdered NiAl coating is now developed in the USSR to combat hot corrosion degradation occurring in vanadate-containing fuel combustion atmospheres [29].

3.5.5 Yttria-Stabilized Zirconia Layers, for both combustion-chamber and aerofoil components [30] are employed as thermal barrier coatings to retard heat flow.

3.6 A comparison of the high-temperature degradation resistance of a range of coating types is given in Figure 5.   In this figure –

(i)   the trends in corrosion resistance for different groups of coatings are indicated by the cross-hatched bands, and

(ii)   the breakdown in the solid curves for the different coatings indicates that the substrate is just penetrated locally.

3.7 Limitations of Coatings

3.7.1 Diffusion Aluminides

These coatings detract to some extent from the mechanical properties of the alloy upon which they are deposited [23].   The formation of the coating itself depends upon diffusion interaction between its constituents and the substrate to form NiAl or CoAl.   Both these intermetallic compounds exhibit inherent brittle behaviour [24], having ductilities of only 0.2 to 0.4 per cent up to about 750°C.   The formation of these compounds, furthermore, reduces the load-bearing cross-sectional area of the component, and this effect can be quite significant in thin-walled components.   The thickness of the coating becomes an important factor when it represents a significant fraction of base metal thickness.   Only in such situations must the coating be considered in any stress calculations;   and this may prove a difficult matter because coatings are generally multicomponent, multilayered materials not necessarily of uniform thickness.

A chronic problem with this type of coating is that it often shows ductile-to-brittle transitions [38], and the transition temperature often depends on the precise atomic composition of the coating.   For example [46], hypostoichiometric β-NiAl undergoes transition at about 760°C,

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whereas hyperstoichiometric (i.e. Al-rich) β-NiAl undergoes transition at
about 980°C.   At low temperatures, where coatings are relatively brittle,
even small strains can cause them to crack and these cracks can propagate
into the alloy.   This will lower the overall tensile strength of the
coating-substrate composite system.   Furthermore, local penetration of
corrosion along these cracks, combined with surface corrosion, can lead to
roughening of the aerofoil surface and a consequent lowering of engine
efficiency.   Above the transition temperature it is unlikely that the
coating will exert a significant influence on the mechanical properties of
the base metal.

The effect of diffusion type coatings on fatigue behaviour of
superalloys is somewhat controversial.   Various workers [see 38] report -

(i)   Diffusion coatings (or the thermal cycles used during
        their application) have a detrimental effect on high-
        temperature fatigue properties.

(ii)   Coating thickness is an important factor: an 0.001-inch
        (0.025 mm) thick coating reduces fatigue strength by about
        10 per cent, while twice this thickness reduces this strength
        by about 15 per cent.

(iii)   Fatigue strength of Nimonic 105 is reduced by aluminizing, but
        this strength can be recovered by suitable heat treatments.

(iv)   In the case of (iii) the coating then adds fatigue life by
        inhibiting substrate 'surface' crack initiation.

Various workers [see 38] agree that aluminized coatings have little
or no detrimental effects on the stress-rupture behaviour of superalloys.

Progressive high-temperature degradation of aluminized coatings does
take place, of course, by various combinations of oxidation, hot corrosion
and alloy-coating interdiffusion.   Cyclic oxidation can cause spalling of
the Al_2O_3 scale which does not always strongly adhere to the NiAl layer,
and this process can continue until the oxide-forming propensity of the
layer is dangerously diminished.   These coatings are not by any means
immune from the variety of hot corrosion propagation mechanisms which have
been discussed in some detail earlier (see section 2.2.2).

3.7.2   M-Cr-Al-Y Overlays

Overlay coatings offer an advantage over diffusion aluminide coatings
in that they cause minimal loss of mechanical properties through diffusion-

consumption and loss of load-bearing section of the substrate.   The
mechanisms of hot corrosion degradation of alloys of these compositions has
also been dealt with above (see section 2.2.2), and this process must be
regarded as the main limitation of this type of coating.

3.7.3 *Other Coatings*

A considerable body of data on the performance of experimental coatings for selected superalloys is scattered in the form of government contract and internal development reports of a number of organizations in the US and UK. Generally, the details of application and the chemical composition of the coatings are not revealed. Consequently, the performance reports from these sources tend to be mere summaries of their experimental observations without many cause-and-effect correlations. An objective review of the available data, therefore, is a difficult and frustrating task, and is not attempted in this paper.

4. NEW CONCEPTS FOR SURFACE MODIFICATION TO

ENHANCE HIGH-TEMPERATURE CORROSION RESISTANCE

4.1 *Introduction*

It is clear that with superalloys the alloying requirements for optimum mechanical properties are significantly different from those for corrosive degradation resistance. Alloys used in the hot parts of modern gas turbine engines are designed primarily for good creep and fatigue resistance coupled with toughness and long-term microstructural stability. The optimal balance of these mechanical properties can be achieved only at the expense of high-temperature corrosion resistance. With very few exceptions, it is consequently necessary to protect the aerofoil components of gas turbine engines with an appropriate coating.

Such protective coatings, however, have significant limitations (refer section 3.7) and, under the most aggressive of hot corrosion conditions such as may be encountered in naval ship propulsion applications, even the most resistant of coatings may not provide periods of component protection which are practical from the logistic and economic points of view. The objective view of present coatings, therefore, must be that they offer purely temporary assistance, and even the new types of coatings (section 3.5) may not offer any real hope for significant improvement in the operating temperature (and hence efficiency, specific fuel consumption, etc.) of gas turbine engines – the real development goal.

A case therefore exists for the detailed examination and critical assessment of new concepts and techniques for imparting enhanced resistance to the high-temperature degradation of superalloy materials and components. This should involve methods which do not rely upon bulk compositional features intended primarily for the control of mechanical properties, or upon the application of protective coatings.

This section of the paper examines, by way of examples, three such concepts each of which embraces new techniques which have not hitherto been

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used for enhancing the high-temperature corrosion resistance of gas turbine components. These concepts and techniques, which appear to have high chances of success, involve –

    (i)   surface alloying

    (ii) optimization of properties of protective oxides, and

    (iii) cathodic protection

4.2 *Surface Alloying*

For reasons given in the introductory section 4.1, it seems reasonable to suggest that the parasurface material of a turbine hot-end component should be regarded as a 'separate' alloy, having the broad compositional features of the bulk but being sufficiently variant in composition to show significantly enhanced resistance to high-temperature corrosion.

Described below are several new surface treatment techniques which can be used to so modify the parasurface composition of an alloy. The examples chosen do not exhaust the list of techniques available for this purpose, but are sufficient to illustrate the practicability of the concept.

4.2.1 *Ion Implantation*

The technique of ion implantation (I.I) consists essentially of the forced introduction of 'foreign' atoms into the parasurface of a solid substrate by bombardment of the solid with ions accelerated in vacuo through an electrical field in the keV to MeV range. The resultant distribution of injected ions, whose concentration reaches a few atomic percent corresponding to implant doses of about 10^{16} ions/cm^2, is well defined [39,40]. This distribution, extending a few μm below the surface, depends on a large number of parameters such as ion energy, ion dose, implantation temperature, substrate crystal orientation and complementary thermally-activated treatments. Several reviews exist [e.g. 39,40] which cover ion beam generation, the physics of implantation, etc, aspects which are beyond the scope of this paper.

The effects of I.I of certain atom species in the enhancement of oxidation resistance are several-fold. It is well known, for example, that small concentrations of certain reactive and rare-earth elements can profoundly retard the rate of thermal oxidation of a metal or alloy. It may be, however, wasteful to introduce such a component throughout the bulk alloy by conventional alloying methods to enhance its oxidation resistance, which is but a parasurface phenomenon; it may even be disastrous to do so because of a detrimental effect upon the bulk properties of the alloy. Furthermore, elements which do not diffuse in or are insoluble in the base alloy can be chosen for I.I. A singular advantage of I.I processing is that it can take place at relatively low temperatures which would affect

bulk mechanical properties but little. This is in contrast to aluminide coating technologies where quite high temperatures are required.

It seems likely that research into the effects of ion-implanted species on high-temperature corrosion processes may have been restrained by the belief that the parasurface alloy produced would be too shallow, or would be rapidly dissipated by diffusion. It is encouraging to find, however, significant evidence to the contrary. For example –

(i) The oxidation behaviour of chromium-rich stainless steels is significantly improved by the implantation of yttrium or rare earth ions [41]. Furthermore, the oxidation behaviour of yttrium-implanted steel compares favourably with that of the corresponding stainless steel containing 0.4 wt.-%Y added throughout the bulk by conventional means.

One hypothesis for this enhanced protection is the formation of impermeable barriers of perovskite structures such as $YCrO_3$ or $LaCrO_3$.

(ii) The resistance to oxidation of titanium at temperatures up to 600°C is markedly improved [42] if the implanted species form stable oxides or perovskite structures (in the case of barium, calcium and europeum implants), binary oxides with titanium or possess a large ionic radius. With barium-implanted titanium, greatly improved oxidation resistance occurs in the presence of the perovskite structure $BaTiO_3$ in the scale.

(iii) The oxidation resistance of Fe-Cr-Al-Y alloys are markedly improved by the implantation of additional aluminium [43,52]. The protection of this alloy is the result of the formation of Al_2O_3, and the implantation of aluminium to a concentration well above the limit permissible in the bulk reduced the rate of oxidation by about an order of magnitude in oxygen at 1200°C.

This and the next example have most significant implications for the enhancement of the degradational resistance of overlay coatings of the M-Cr-Al-Y kind.

(iv) The implantation of cerium into Fe-Cr-Al alloys greatly decreases the rate of spallation of the protective oxides formed [44].

(v) A stainless-type copper is produced by implanting aluminium, titanium or chromium (the latter a normally insoluble element) into copper [43].

(vi) The oxidation kinetics of Ti-6Al-4V at 600°C are slowed by about an order of magnitude by the implantation of barium or calcium [45].

Broadly, it is possible to prescribe ways in which the I.I process enhances the efficacy of various mechanisms which govern the protective properties of oxide scales.   These ways would include -

(i) the reduction, by doping, of the concentration of defects such as cation vacancies in oxide scales which govern mass transport through such scales,

(ii) the injection of dopant impurities into the alloy parasurface which could block metal ion migration paths of the short-circuit kind,

(iii) the increase in the concentration, at the alloy surface, of elements known to enhance the adhesion of scales. These elements include yttrium, cerium, calcium, and magnesium, and

(iv) the favourable influencing of the mechanical properties of scales, by utilizing known compositional dependences, to lessen compressive growth stresses, to reduce the energy for the propagation of dislocations in stress relief, etc.

It seems reasonable to assert that I.I has high potential as a feasible method of treating finished components to enhance their resistance to high-temperature degradation by oxidation and hot corrosion.   Its practicability may well depend upon the ultimate economics of the process.   It has been envisaged [40] that, in the first instance, I.I could well be applied in the production of small corrosion resistant components for use where high standards of performance are essential for reasons of safety or the cost of replacement.   Aerofoil components of gas turbine engines seem an ideal example.

4.2.2   Laser Surface Alloying

Surface interactions using directed laser beams have attracted much interest in recent times.   Thus in metals the phenomenon of 'laser glazing', in which the metal surface is scanned by a high-power laser beam to rapidly induce a thin molten surface layer, is applied to influence mechanical properties.   Fatigue crack initiation, for example [47], can be reduced by lasers using modest power densities between 1 and 10 MW/cm^2. If the beam is scanned across the metal surface at a rate which produces surface melting and rapid solidification whilst avoiding vaporization, then fine-grain metallurgical structures can be produced extending to depths of up to 30 μm.

If this technique, which ought also to enhance resistance to corrosion fatigue, is extended to include the introduction of alloying elements to the molten pool, then a laser surface alloying method is at hand.   The melt depth will limit the initial diffusion depth of the surface alloying elements, so that the depth of initial surface alloying will be governed by the power and sweep rate of the laser.

The very rapid heating and cooling rates of the surface alloy layer
allow a considerable broadening of normal alloying concepts. In
particular, solubility limits would not be a primary restriction and, as
with ion implantation, even normally 'insoluble' elements could be added to
the melt layer. These insoluble elements and/or resulting compounds would
presumably occupy interdendritic sites in the extremely fine dendritic
structures which these laser techniques would produce, and the properties
of this type of structure would need to be ascertained.

It has been demonstrated [48] that alloy and refractory oxide powder
particles can be injected into high-energy laser beams, melted and
propelled downstream toward a metallic substrate. Presumably, a feasible
development would be to use the same laser beam to produce the substrate
melt into which alloy particles could be injected. It would seem that, in
air, forces exerted on the alloying powder particles are approximately
linearly proportional to the power density of the laser beam. In air,
viscous drag would limit particle velocity, but drag would decrease and
particle velocity increase as the air pressure was decreased.

Other methods could be used to introduce the desired elemental
components to the laser-melted surface alloy. For example, the required
modifying elements could be deposited in a thin layer on the substrate by
an ion plating method [47] preferably sputter ion plating. Laser-beam
melting of the plated layer plus some of the substrate would then produce a
corrosion resistant surface alloy of the required component concentration
ratio.

4.2.3 Irradiation-Induced Surface Segregation

In section 3 - Coatings - the superior oxidation resistance of
certain intermetallic compounds of nickel, notably nickel aluminide, NiAl,
is discussed at length, while the potential of other such compounds,
particularly nickel silicide, Ni_3Si, in protective coating systems is
alluded to.

The surface alloying effect of radiation-induced segregation in
dilute Ni-Si alloys has been studied [49] after irradiation at 525°C with
3 MeV $^{58}Ni^+$. Profiles of alloy composition as a function of depth from the
irradiated surface were obtained and rapid segregation of silicon toward
the irradiated surface was observed. The solubility limit of silicon in
nickel was reached at the surface after which the intermetallic compound
Ni_3Si was precipitated.

Turning now to the second of the new concepts for surface
modification for the enhancement of high-temperature corrosion resistance,
namely the optimization of the properties of oxides which govern their
protective efficacy, the example chosen for discussion is -

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4.3 Thermal Passivation

Thermal Passivation is a newly proposed method [35] of enhancing the oxidation resistance of metallic alloys for high-temperature service. It is based upon the concept that the high-temperature oxidation resistance of a metallic material is primarily dependent upon the degree to which its oxide scale inhibits the counterdiffusion of the species reacting to produce it. Properties of protective scales, therefore, must include a minimal concentration of ionic defects which affect transport through it, a high density, and freedom from pores and cracks which allow short-circuit diffusion. Other necessary properties include low vapour pressure and low reactivity with respect to a particular environment.

Thermal Passivation aims at producing protective oxides which exhibit these properties to the highest possible degree. Analysis of the problem [35] indicates that the following procedures are involved –

(i) selection of a solute component element which will produce, in the relevant ranges of temperature and oxygen pressure, a stable and inert oxide of near stoichiometric composition;

(ii) calculation of the theoretical critical concentration of the selected solute at which the transition from internal to external modes of oxidation will occur, i.e. the concentration above which the oxide of this solute will form only on the surface of the alloy; and

(iii) determination of the parameters of high temperature and low oxygen pressure within which exclusive selective oxidation will occur to produce (in a special thermal pre-treatment) a single passive thin-film of the preferred surface oxide.

These procedures are discussed briefly in turn –

4.3.1 Selection of a Suitable Oxide

The first requirement is that the oxide will have high thermodynamic stability, of which its negative free energy of formation is the measure. Table 2 lists oxides of interest in magnitude order of this energy. It will be seen that alumina, Al_2O_3, an important protective oxide on superalloys, has a relatively high negative free energy of formation, but that there are quite a number of oxides with higher values.

Second, the ability of an oxide to inhibit the counterdiffusion of species reacting to produce it (i.e. to inhibit oxidation) is largely governed by the concentration of its point defects such as vacancies. Highly stoichiometric oxides, which have low defect concentrations, are the most inhibitive of diffusion. The defect concentration in an oxide is proportional to its electrical conductivity, which reflects the mechanism of diffusion by ionic and electronic transport. Table 2 also classifies

the oxides of interest in terms of their electrical conductivities.   It
will be seen that of the oxides which the major solute element components
of superalloys produce, the oxide of aluminium, Al_2O_3, has an extremely low
conductivity as does the oxide of silicon, SiO_2, whilst that of chromium,
Cr_2O_3, has only a moderately low conductivity.   Of special interest is the
fact that some oxides, Y_2O_3, ThO_2, Ce_2O_3, MgO, BeO, HfO_2 and ZrO_2, although
having very low electrical conductivities, do not normally feature in
protective oxide systems on superalloys.

Third, it seems important to note that low electrical conductivity
implies a large energy gap between the electronic conduction and valence
bands.   As the formation of lattice defects generally involves an
ionization process the existence of a large gap probably implies a large
energy of formation of lattice defects, that is, a high resistance to the
formation of structural characteristics which encourage diffusion and
oxidation progress.

4.3.2   Transition Concentration: Internal to External Oxidation

The second requirement for Thermal Passivation is that the high-
stability oxide chosen must form exclusively on the surface to act as a
highly efficacious diffusion barrier.   It is thus necessary to calculate
the theoretical critical concentration of the selected solute at which the
transition from internal to external modes of oxidation occur.

The basic method [36] of calculation of this critical concentration,
N_B, of binary solute B in a dilute solid solution alloy A-B above which, at
a given temperature and pressure of oxygen, its oxide is formed exclusively
on the surface, is given by the relationship

$$N_B = L \left(\pi k_p / D \right)^{1/2}$$

where k_p = the parabolic rate constant for the exclusive
formation of B oxide

D = diffusion coefficient of B in the alloy

L = (a constant) = $\dfrac{V}{Z_B M_0}$

where V = molar volume of the alloy

Z_B = valence of solute atoms

M_0 = atomic weight of oxygen

Using this relationship for the more important solutes in high-
temperature alloys and for the base nickel, it is found that for the three
binary alloys listed below the critical internal/external oxidation
transition concentrations (in air at 1000°C) are –

	atoms per cent	weight per cent
Ni-Cr	12	13-1/2
Ni-Al	9	3-1/2
Ni-Si	8	4

It can be seen that many high-temperature alloys have solute concentrations of the same general magnitude as those values shown above, and are hence potentially able to be thermally passivated.

The extension of this method to the estimation of internal/external oxidation transition concentrations in alloys more complex than binary involves, in addition, experimental verification involving variation of the concentration of the solute of interest in a complex base of fixed composition. The transitional concentration in the complex alloy is generally somewhat less than in the binary case, so that the binary-related calculation above provides a very good starting value where experimentation is necessary.

4.3.3 Exclusive Preferential Oxidation

The third important procedure in Thermal Passivation involves the actual production of the chosen, stable, inert and highly stoichiometric oxide layer as a discrete passive film exclusively on the surface of the alloy. This requires a determination of the parametric bounds of high temperature and low oxygen pressure within which the chosen oxide film will form preferentially to the exclusion of all others.

Resort to the appropriate thermodynamic data facilitates the choice of the appropriate temperatures and pressures. Figure 6 shows the relevant reaction equilibria in terms of the dissociation pressure/temperature relationships for some of the main oxides involved. It is clear, for example, that in the regime marked 'D' the exclusive oxidation of aluminium will occur in a complex Ni-Cr-Si-Al alloy.

It is to be noted that the oxygen pressures of interest are extremely low and not able to be attained in 'industrial' vacua. It has been found, however, that the required low oxygen pressures can readily be achieved in an atmosphere of hydrogen and water vapour [37].

4.4 Cathodic Protection

The basic behaviour of oxide scales in high-temperature oxidation is analogous to that of aqueous electrolytes in wet corrosion; oxides can thus be regarded as high-temperature electrolytes in that their defective structures permit diffusion processes involving the transport of electrical charges in the form of ions and electrons. Oxides which form on superalloys exhibit, in fact, significant electrical conductivity at elevated temperatures.

In principle, therefore, cathodic protection of metals against high-temperature corrosion is feasible. Cathodic protection can be defined as having been established when the potential of the cathodic sites on a metal surface has been lowered, by a polarizing current from either an extrinsic source (generator) or an intrinsic source (sacrificial anode) to the open circuit potential of the anodic sites on the surface.

The proposition that superalloys are amenable to cathodic protection against high-temperature oxidation appears to have already been demonstrated

  (i)   in the case of chromia and alumina forming alloys by
        the application of a protective current (extrinsic
        source) [50], and

  (ii) in the case of the pairing of dissimilar chromia and
        silica forming alloys in mutual contact with each other
        and the conjoint scale (intrinsic source) [51].

The latter case has particular significance to the multiple examples of dissimilar alloys in contact in gas turbine engines.

5. CONCLUSIONS

5.1 As is abundantly clear, even when a unified view of the subject is taken as in this paper, that the hot corrosion of multicomponent alloys is a phenomenon of the utmost complexity. In recent years substantial progress has been made toward a more complete understanding of the underlying mechanisms involved. It seems clear [19] that continued progress will be facilitated if hot corrosion is looked upon as occurring in two stages, an initiation stage (see section 2.2.1) and a propagation stage (see section 2.2.2). Furthermore, the effects produced by different elements on the hot corrosion process should be qualified as to whether the effect occurs in the initiation stage or the propagation stage, and if the propagation stage, for which propagation mode. In the refining of existing models for hot corrosion mechanisms, fruitful areas of research might well include –

  (a)   more exact definition of the interacting roles of
        oxide fluxing and mechanical damage,

  (b)   establishment of the means for improving the
        resistance of protective scales to the initiation
        process (e.g. section 4.3),

  (c)   more precise knowledge of the mechanisms whereby
        elements such as titanium (in alloys) and platinum
        (in coatings) exert their beneficial effects,

  (d)   more extensive studies of the hot corrosion of

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potentially useful ceramic materials such as silicon
carbide, silicon nitride and zirconium oxide, and

(e) the protective potential of the surface modification
techniques such as ion implantation, discussed in
section 4.

5.2 There is no doubt that the coatings discussed in section 3 of this
paper play a vital and effective role in maintaining the surface integrity
of modern superalloys. As service conditions become more severe (higher
temperatures and more aggressive environments), however, new and enhanced
protective systems are essential [38].

Despite the undoubted advances made in the development of coating
systems in recent years, much of the progress has resulted from enlightened
empiricism, and a number of fundamental questions remain unanswered.
Although, for example, alloying elements are known to control thermodynamic
stability, diffusional characteristics, morphology, and the distribution of
phases in coatings (and ultimately their protective abilities), relevant
cause-and-effect mechanisms are not at all fully understood. Similarly,
because of inadequate understanding of mass transfer processes and the
chemical reactions involved in coating formation, inadequate control of
coating quality at the fabrication stage is the likely result.
Considerable scope must exist for study of more fundamental aspects of the
modes of formation, the properties and behaviours, and the degradational
mechanisms of existing and new coating varieties.

Some types of coating warrant greater investigation, including those
forming oxygen compounds other than alumina; for example, the protective
propensities of silica, silicates, perovskites, and also of intermetallic
compounds between elemental components of the alloys and noble metals seem
high. Furthermore it seems anomalous that, whilst considerable attention
is now focussed on the development of tough ceramics for turbine components
[e.g. 2], a viable ceramic coating does not appear to have emerged.

5.3 Keys to the further improvement of new and existing coatings, as well
as of the superalloys themselves, may well be found amongst the new
concepts of surface modification dealt with in section 4. Beneficial
surface alloying, the enhancement of the diffusion-inhibiting propensity
and adhesion of oxides, in particular, seem bound to produce worthwhile
dividends for coating technology.

Attention is drawn to these new concepts and to the principal new
techniques which facilitate their application, in particular ion
implantation, laser surface alloying and thermal passivation.

6. ACKNOWLEDGEMENTS

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T A B L E 2

VITAL PROPERTIES OF OXIDES

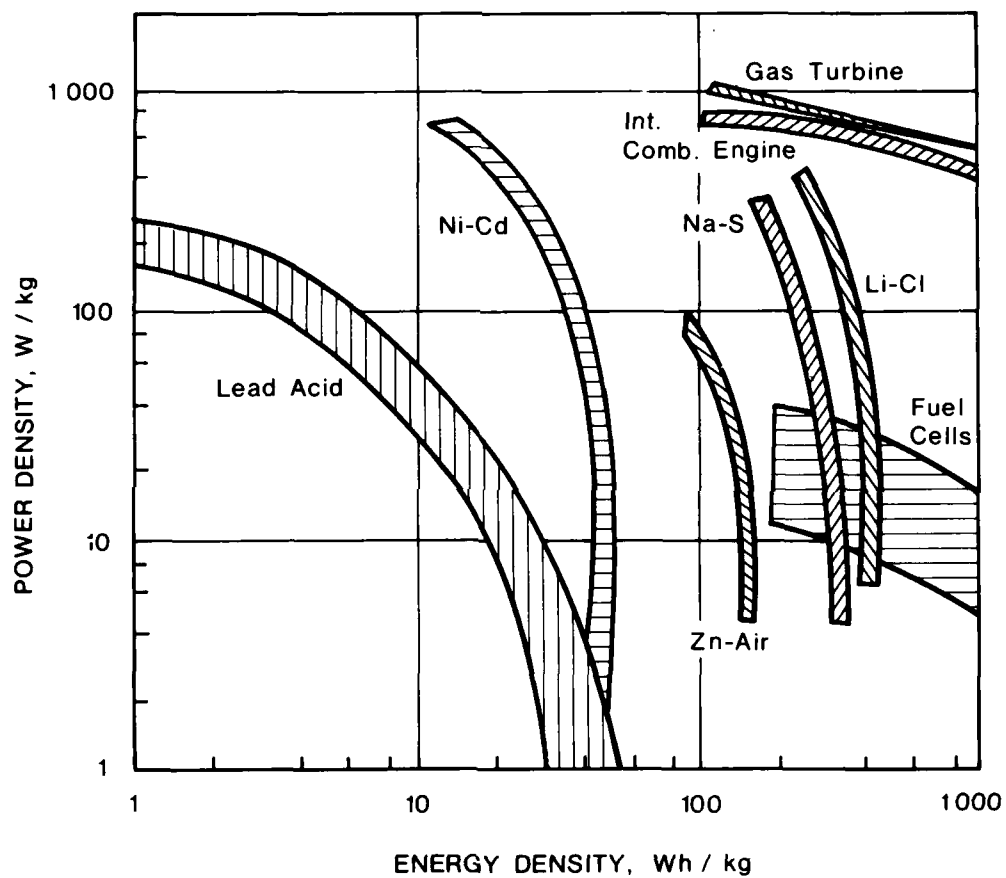| Oxide		Free Energy of Formation at 298 K $kJ\ mol\ O^{-1}$	Electrical Conductivity at 1273 K $ohm^{-1}cm^{-1}$	Band Gap eV
CaO		-603	10^{-4}	6.5
ThO_2		579	10^{-3}	
Ce_2O_3		562		
BeO		559	10^{-7}	
MgO		558	2×10^{-7}	7.3
Y_2O_3		546		
HfO_2		517		
Al_2O_3	*	-516	10^{-7}	7.0
ZrO_2		509	10^{-5}	
TiO_2	*	435	2×10^{-2}	3.1
SiO_2	*	419	10^{-6}	
Ta_2O_5		386		
Cr_2O_3	*	341	2×10^{-1}	
FeO		-263	5×10^{3}	
NiO	*	238	10^{-2}	2.3
CoO	*	234	10^{-1}	
Cu_2O		164	5×10^{2}	2.2

* contained e.g. in NIMONIC 105

FIG. 1 — Operating characteristics of gas turbines
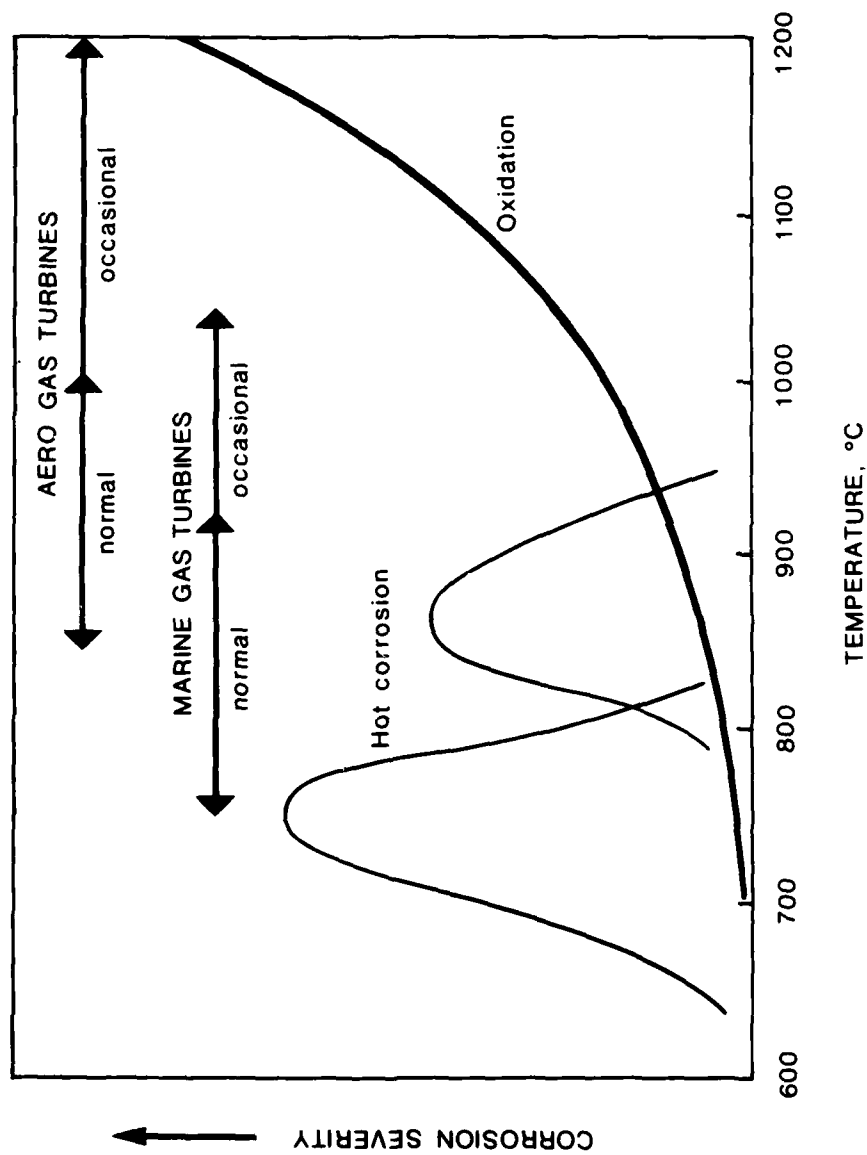and some other energy sources (after
Coe [1]).

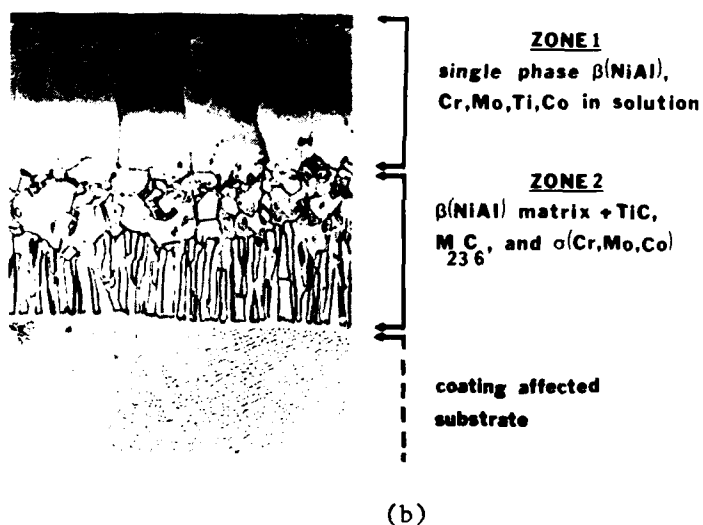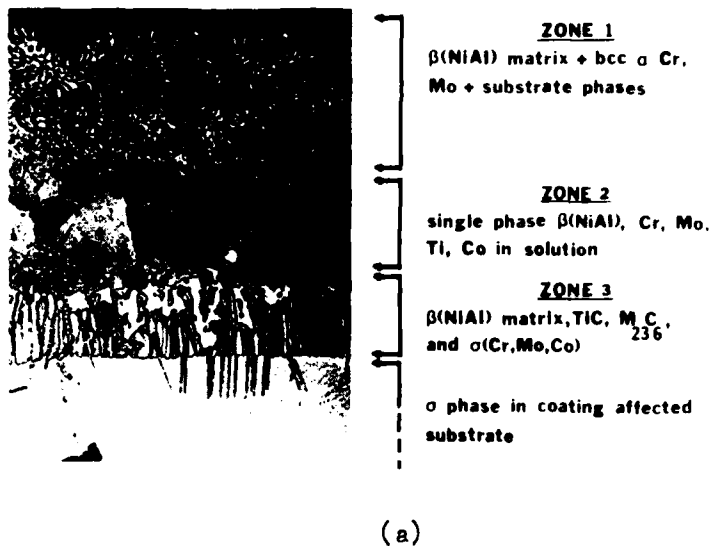FIG. 2 — General Relationships in Gas Turbine Corrosion

ZONE 1
β(NiAl) matrix + bcc σ Cr,
Mo + substrate phases

ZONE 2
single phase β(NiAl), Cr, Mo.
Ti, Co in solution

ZONE 3
β(NiAl) matrix, TiC, $M_{23}C_6$,
and σ(Cr,Mo,Co)

σ phase in coating affected
substrate

(a)

ZONE 1
single phase β(NiAl),
Cr,Mo,Ti,Co in solution

ZONE 2
β(NiAl) matrix + TiC,
$M_{23}C_6$, and σ(Cr,Mo,Co)

coating affected
substrate

(b)

FIG. 3 — Microstructures and phase identities in aluminide coatings
on UDIMET 700. X1000 and reduced 35% for reproduction.

(a) inward-diffusion type coating formed by a high-aluminium
activity process followed by heat-treatment for 4h at
1080°C.

(b) outward-diffusion type coating formed by a high activity
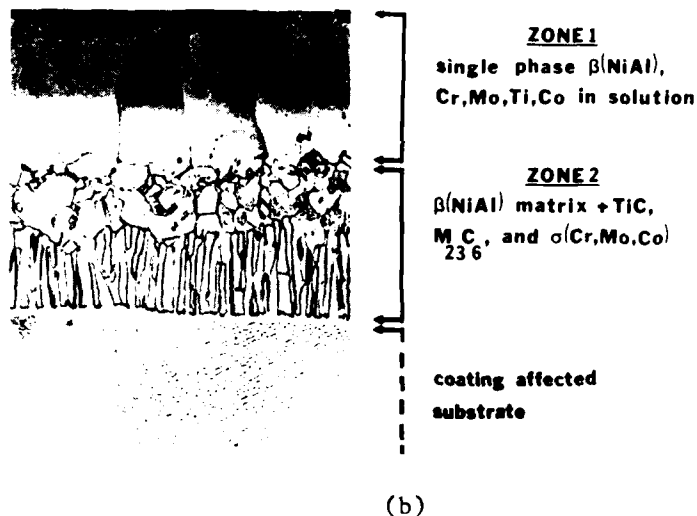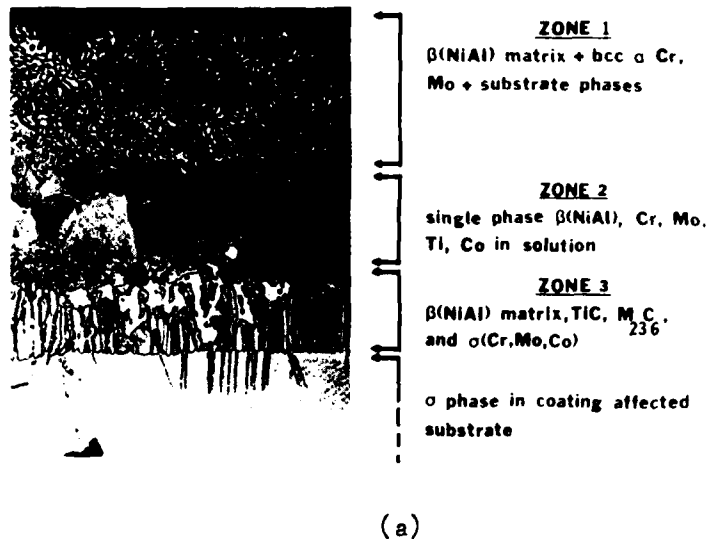process. (After Goward et al [24]).

ZONE 1
β(NiAl) matrix + bcc α Cr,
Mo + substrate phases

ZONE 2
single phase β(NiAl), Cr, Mo,
Ti, Co in solution

ZONE 3
β(NiAl) matrix, TiC, $M_{23}C_6$,
and σ(Cr,Mo,Co)

σ phase in coating affected
substrate

(a)

ZONE 1
single phase β(NiAl),
Cr,Mo,Ti,Co in solution

ZONE 2
β(NiAl) matrix + TiC,
$M_{23}C_6$, and σ(Cr,Mo,Co)

coating affected
substrate

(b)

FIG. 3 — Microstructures and phase identities in aluminide coatings
on UDIMET 700.   X1000 and reduced 35% for reproduction.

(a) inward-diffusion type coating formed by a high-aluminium
activity process followed by heat-treatment for 4h at
1080°C.

(b) outward-diffusion type coating formed by a high activity
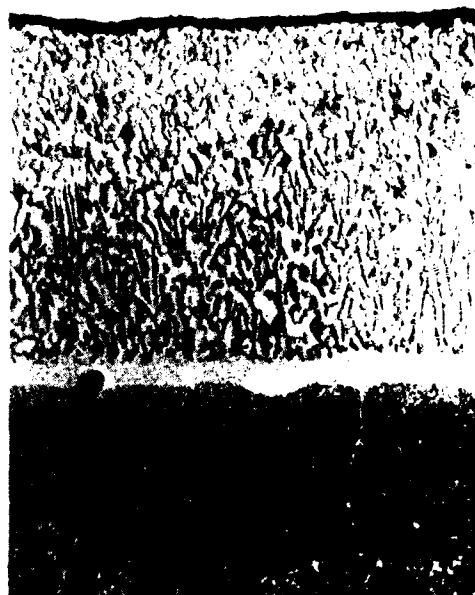process. (After Goward et al [24]).

FIG. 4 — Microstructure and phase identities in a typical
overlay-type coating, specifically CoCrAlY (after
Goward [54]).
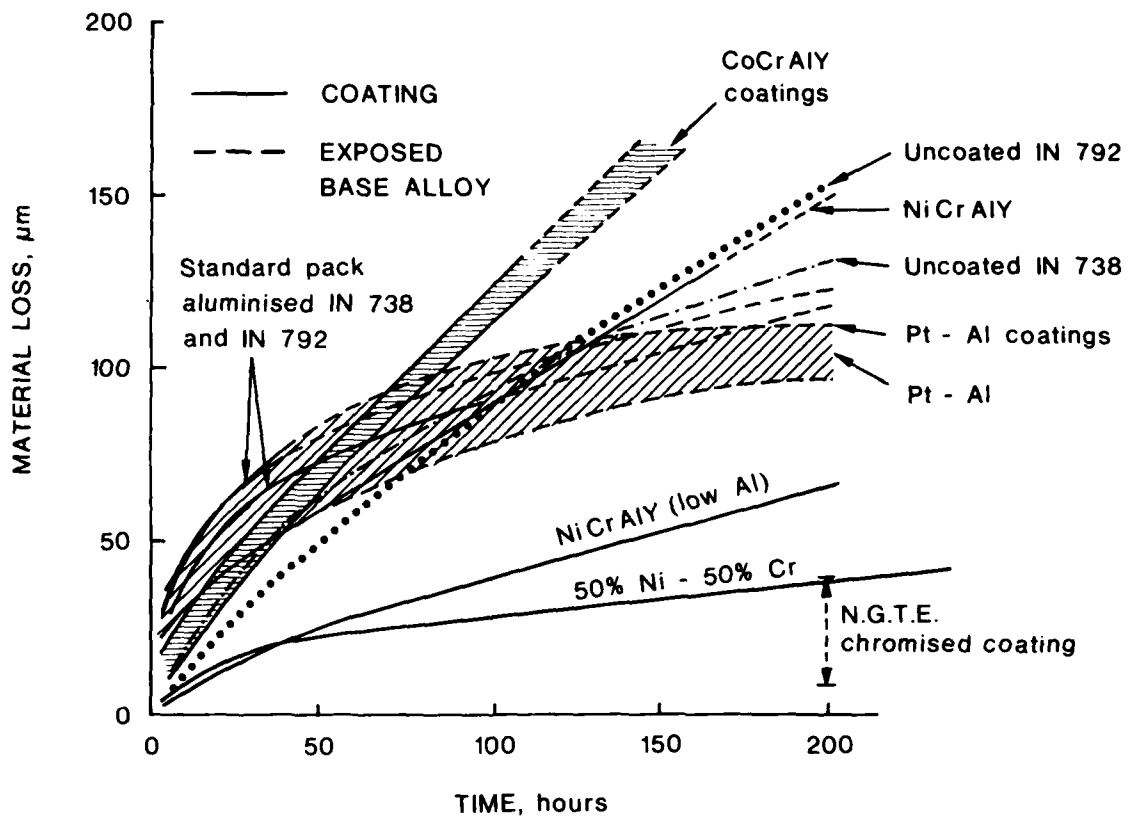(The outer coating comprises Co γ S.S. matrix
plus β CoAl)

FIG. 5 — Corrosion test data; material loss as a function
of time for various alloys and coatings (after
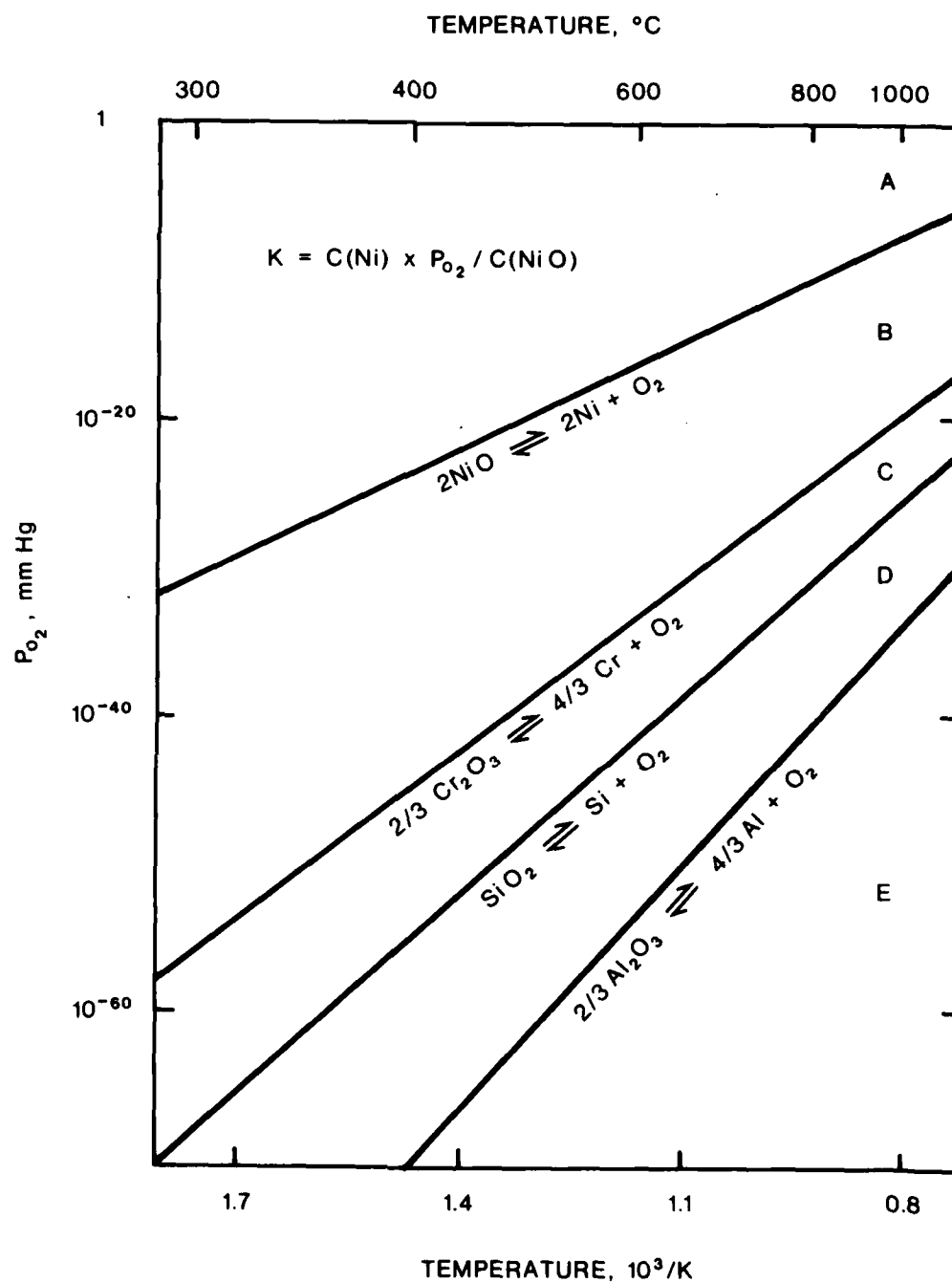Restall [23]).

TEMPERATURE, °C

FIG. 6 – Reaction equilibria: relation between P_{O_2} and temperature (1 mmHg = 133.3 Pa). (after Burley [53]).

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